Chemical Fluid Deposition Enables Conformal Coating of High-Aspect-Ratio Features in Si Wafers

The increasing miniaturization of microelectronic devices has put heavy demands on the technologies used to produce them. For example, as the width of interconnect features in integrated circuits approaches 100 nm, conventional deposition techniques may be insufficient to uniformly fill these high-aspect-ratio channels with copper. Current Cu metallization techniques based on electrolytic plating require a conformal seed layer prior to feature fill. These seed layers are deposited using line-of-sight physical vapor deposition techniques that become limited in small, high-aspect-ratio features. An alternative is to use chemical vapor deposition (CVD). The relatively low vapor pressures of the organometallic precursors used in CVD, however, produce mass-transport limitations that can lead to nonuniform deposition of metal in the channels, resulting in faulty connections between functional devices on a chip.

To overcome these limitations, researchers at the University of Massachusetts have developed a technique called chemical fluid deposition (CFD), which involves organometallic precursors dissolved in supercritical CO_2 (sc-CO_2). As reported by J. Blackburn and co-workers in the October 5 issue of *Science*, CFD provides a precursor concentration of up to 3 orders of magnitude greater than CVD, while maintaining transport properties that are similar to those of a gas; this combination allows rapid diffusion of the organometallic into the narrow channels, promoting a uniform conformal coating. The addition of hydrogen gas, which is miscible in sc-CO_2, then reduces the precursor to its metallic state, the researchers said.

Silicon test wafers were placed in a cold-walled high-pressure reactor vessel at a pressure of 200 atm. The silicon substrate was resistively heated to temperatures ranging from 175°C to 200°C in sc-CO_2 solutions containing Cu(II) bishexafluoroacetylacetonate [Cu(hfac)$_2$] or Cu(II) tetramethylheptanedionate [Cu(tmhd)$_2$]. Copper was deposited by hydrogen reduction exclusively on Ni films or small Pd seed clusters. By raising the temperature to 250°C, the researchers were able to deposit metallic Cu from Cu(tmhd)$_2$ directly onto the native silicon oxide surface in a single step, without the need for seed crystals. Cu(tmhd)$_2$ provides the option of a nonfluorinated precursor, which reduces environmental concerns, according to the research team. The deposited films were continuous, highly reflective, and essentially free of impurities.

The researchers also deposited nickel onto Pd seed clusters from a solution of bis(cyclopentadienyl)nickel ($NiCp_2$) in sc-CO_2 in a hot-walled reactor at 60°C and 200 atm in the presence of hydrogen. They said that raising the temperature to 120°C eliminated the need for seed clusters.

For both Cu and Ni, scanning electron microscopy images revealed conformal coating of 100-nm-wide by 800-nm-deep channels etched in silicon wafers, the researchers said. Furthermore, they said, secondary-ion mass spectrometry analysis showed the deposited films to be sufficiently pure, and resistivity measurements were well within specifications for Cu interconnect structures.

TIM PALUCKA

Antireflection Microstructures Achieved with F_2-Doped SiO_2 Films

Sub-wavelength-structured (SWS) surfaces with surface-relief gratings with a period smaller than the wavelength of light have received increased interest for their potential in applications such as waveguides, optical fibers, and electro-optical materials. Among the SWS surfaces, antireflective coatings are generally obtained in glass by treating the surface with acid, a process that leads to a gradual change in the refractive index and a measurable decrease of reflection at the surface, equivalent to that of a multilayered antireflective coating. In the November 1 issue of *Optics Letters*, a team of researchers in Japan from the National Institute of Advanced Industrial Science and Technology, Osaka Prefecture University, and Samco International reported on their fabrication technique for SWS surfaces, which uses a fluorine-doped SiO_2 film.

The researchers obtained fluorine-doped SiO_2 by a plasma-enhanced chemical vapor deposition system with $Si(OC_2H_5)_4$ and CF_4 as raw materials. They controlled the content of the fluorine in the film by controlling the flow rate of the CF_4. After deposition, the films were etched in a 5%-diluted HF solution at 25°C. To obtain the two-dimensional (2D) periodic antireflective structures, a six-layer film of F_2-doped SiO_2 was deposited on a SiO_2 substrate. Each layer was 0.2 μm, and the content of F_2 was varied at 0, 6, 7, 8, and 9 mol% in the six layers from the depth to the surface, respectively. Then the surface of the film was coated onto a 1-μm photoresist and exposed in two steps to a 325-nm-wavelength He-Co laser, resulting in a 2D holed pattern with a period of 1 μm that was further coated with a 0.2-μm chromium film. Further processing of the samples consisted of the removal of the photoresist, vertical dry etching in CHF_3, and further etching in a 5%-diluted HF solution for 25 s at 25°C. The result was a cylindrical profile that became a cone profile after the wet etching, with sharp tips and grooves ~1.0 μm deep. The researchers reported a maximum transmittance of 95.8% at a wavelength of 1.85 μm, giving an estimated 0.7% reflectance for the cone-shaped microstructure, corresponding to one-fifth of the Fresnel reflection at the flat SiO_2 surface.

With this method, the researchers anticipate the fabrication of SWS surfaces with deeper grooves and shorter periods, which will lead to antireflection effects for shorter wavelengths. Precise control of the grating aspect ratio is possible by charging the F_2-content profile in the films.

IULIA MUNTELE

Ink-Jet Printing Explored for Fabricating Devices and Materials

University of Arizona researcher Paul Calvert and his collaborators at Sandia National Laboratories are using ink-jet printing to fabricate various organic or inorganic films for electronic devices and sensors. Some of the results on ionic self-assembly of ink-jet-printed polymer films appear in a recent issue of *Polymeric Materials: Science & Engineering* for research done in collaboration with Mousa Ghaemi of Mazandaran University in Iran. A detailed overview of the method by P. Calvert can be found in *Chem. Mater.* **13** (2001) p. 3299.

Ink-jet printing is a highly developed technique for making images. It is now being explored in the printing of devices, especially where organic and inorganic components are combined. The typical examples include organic light-emitting diodes (OLEDs), biochemical sensors, and electronics on flexible substrates. However, the realization of a complex, multilayered, multimaterial device structure requires solutions to a number of problems related to compatibility and reactivity among the substrate and materials being deposited.

To get higher resolutions, the researchers explored depositing gels by inkjet printing and subsequently treating the gel layers with mineralizing solutions. They used a modified HP Deskjet printer to deposit dilute solutions of polydimethyldiallylammonium chloride and polystyrenesulfonate sequentially onto glass slides. The slides were wet-annealed at 70°C over a water reservoir, and the polymers self-assembled into an insoluble layer of gel. The same approach allows for submicrometer Al_2O_3 particles to be dispersed into the anionic polymer solution. Overprinting with the cationic polymer forms an alumina film bound by a cation/anion gel. Diepoxide/amine sub-

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